K₂Cr₈O₁₆ predicted as a half-metallic ferromagnet: Scenario for a metal-insulator transition

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Based on the first-principles electronic structure calculations, we predict that a chromium oxide $K_2Cr_8O_{16}$ of hollandite type should be a half-metallic ferromagnet where the Fermi level crosses only the majority-spin band, whereas the minority-spin band has a semiconducting gap. We show that the double-exchange mechanism is responsible for the observed saturated ferromagnetism. We discuss possible scenarios of the metal-insulator transition observed at low temperature and we argue that the formation of the incommensurate long-wavelength density wave of spinless fermions caused by the Fermi-surface nesting may be the origin of the opening of the charge gap.

I. INTRODUCTION

Half-metallic ferromagnets[1] offer a unique opportunity for studying the electronic states of strongly correlated electron systems. Here, only the majority-spin electrons form the Fermi surface with a gapped minority-spin band[2] and can couple with excitations of the spin (and in some cases orbital) degrees of freedom of the system. The situation therefore should attract much interest, in particular, when the relevant electrons are strongly correlated, leading the system to double-exchange ferromagnetism[3] and metal-insulator transition (MIT). In this paper, we will show that a chromium oxide $K_2Cr_8O_{16}$ with the hollandite-type crystal structure[4,5] belongs to this class of materials and can provide a good opportunity for further development of the physics of strong electron correlations.

The crystal structure of $K_2Cr_8O_{16}$ (see Fig. 1) belongs to a group of hollandite-type phases where one-dimensional (1D) double strings of edge-shared CrO_6 octahedra forms a Cr_8O_{16} framework of a tunnel structure, wherein K ions reside.[6] Cr ions are in the mixed-valent state of $Cr^{4+}(d^2)$: $Cr^{3+}(d^3)=3:1$, and hence with 2.25 electrons per Cr ion. It has recently been reported[7] that the phase transition from the Pauli-paramagnetic metal to ferromagnetic metal occurs at $T_c \simeq 180$ K by lowering temperatures, where the ferromagnetic state has a full spin polarization of $18\mu_B$ per formula unit (f.u.) at low temperatures, which is a realization of saturated ferromagnetism.

In addition to this phase transition, it has also been reported[7] that another phase transition occurs from the ferromagnetic metal to ferromagnetic insulator at $T_{MI} \simeq 95$ K, suggesting that the charge gap opens below T_{MI}. Surprisingly, the spin polarization is hardly affected by this MIT and no structural distortions associated with this MIT have been observed so far.[7] The mechanism of the MIT of this material has therefore been a great puzzle.

In this paper, we perform the first-principles electronic structure calculations based on the generalized gradient approximation (GGA) in the density-functional theory and we predict that the materials $A_2Cr_8O_{16}$ (A=K and Rb) belong to a class of half-metallic ferromagnets, i.e., the majority-spin electrons are metallic, whereas the minority-spin electrons are semiconducting with a band gap. We also show from the GGA and GGA+U calculations that the double-exchange mechanism is responsible for the observed saturated ferromagnetism. We then discuss possible mechanisms of the MIT of this material and argue that the formation of an incommensurate long-wavelength spin and charge density waves (DW) due to Fermi-surface nesting may be the origin of the MIT of this material. The opening of the gap in the majority-spin band should, however, be detrimental to the double-exchange ferromagnetism, for which we consider possible reconciliations. We hope that our results will encourage further experimental studies of this intriguing material.

This paper is organized as follows: in Sec. II, we show our method of calculations. In Sec. III, we present our results of the calculations, and discuss the origin of ferromagnetism and possible mechanisms of the MIT of $K_2Cr_8O_{16}$. Summary of our work and prospects for future studies are given in Sec. IV.
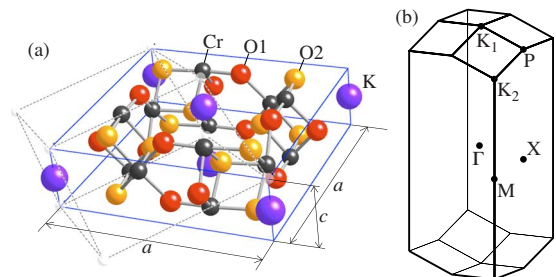

FIG. 1. (Color online) Schematic representation of (a) the unit cell of the body-centered tetragonal lattice (solid lines) and (b) Brillouin zone of $K_2Cr_8O_{16}$. In (a), the primitive unit cell is also shown in the thin dotted lines. In (b), the symbols represent $\Gamma(0,0,0)$, $M(2\pi/a,0,0)$, $X(\pi/a,\pi/a,0)$, $P(\pi/a,\pi/a,\pi/c)$, $K_1[0,0,\pi(1/c+c/a^2)]$, and $K_2[2\pi/a,0,\pi(1/c-c/a^2)]$, where K_1 and K_2 are equivalent.
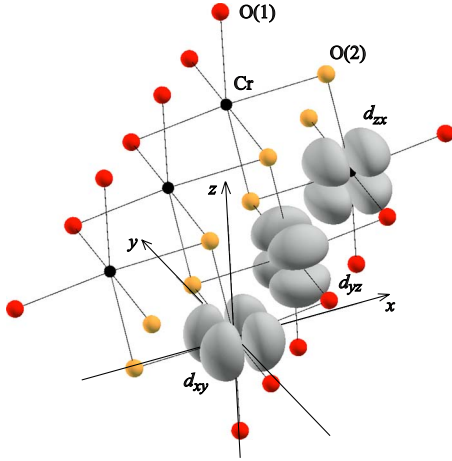
FIG. 2. (Color online) Schematic representations of the local structure of $K_2Cr_8O_{16}$, together with the three t_{2g} orbitals d_{xy}, d_{yz}, and d_{zx} of Cr ions in the xyz-coordinate system. There are two inequivalent O sites, O(1) and O(2). All the Cr sites are equivalent.

II. METHOD OF CALCULATION

The electronic structure calculation in GGA is carried out by employing the computer code WIEN2K,[8] which is based on the full-potential linearized augmented-plane-wave method. We use the exchange-correlation potential of Ref. [9]. The spin polarization is allowed. The spin-orbit interaction is not taken into account. We use 1221 $\boldsymbol{k}$ points in the irreducible part of the Brillouin zone in the self-consistent calculations. We use the plane-wave cutoff of $K_{max}=4.24$ bohr^{-1}. The GGA+U calculation[10] is also made to see the effects of on-site electron correlation U on the band structure. We assume the experimental crystal structure of $K_2Cr_8O_{16}$ observed at room temperature with the lattice constants of $a=9.7627$ and $c=2.9347$ Å.[6] The Bravais lattice is body-centered tetragonal and the primitive unit cell (u.c.) contains four Cr ions, one K ion, and eight O ions, i.e., KCr_4O_8. The local structure around Cr ions is shown in Fig. [2]. We use the code XCRYSDEN (Ref. [11]) for graphical purposes.

III. RESULTS AND DISCUSSION

A. Ground state

The total ground-state energies obtained in GGA are $-10\,816.1918$ Ry/u.c. in the ferromagnetic state and $-10\,815.9597$ Ry/u.c. in the paramagnetic state, resulting in the energy gain of 3.16 eV/u.c. due to stabilization by the spin polarization, which is realized already in the GGA level. In the ground state, we have the full spin polarization with the magnetic moment of $9.000\mu_B$/u.c., which consists of the contributions from Cr ions, $2.043\mu_B$/atom, O(1) ions, $0.014\mu_B$/atom, and O(2) ions, $-0.082\mu_B$/atom, in the atomic spheres, and $1.098\mu_B$/u.c., in the interstitial region. Note that the O(2) ions inside the double strings of Cr ions have a negative spin polarization, whereas the O(1) ions connecting the double strings have a positive spin polarization.

B. Density of states

The calculated density of states (DOS) is shown in Fig. [3] in a wide energy range covering over the O 2p
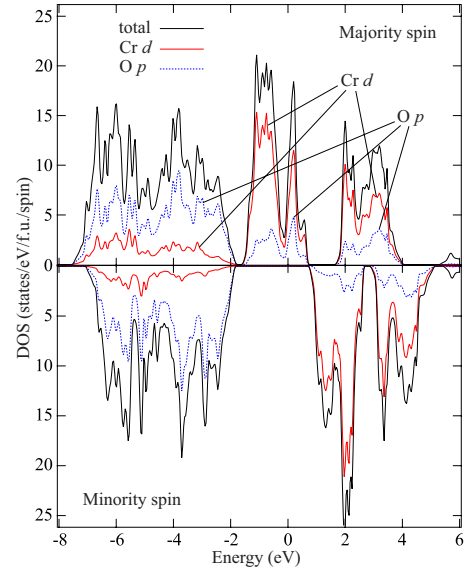

FIG. 3. (Color online) Calculated result for the DOS [per spin per formula unit (f.u.)] of $K_2Cr_8O_{16}$ in a wide energy range for the ferromagnetic state. The Fermi level is set to be the origin of energy.

and Cr 3d bands. We find three separate peaks in both the majority- and minority-spin bands: in the majority (minority) spin band, the O 2p weight is located mainly at $-7.5 \lesssim \varepsilon \lesssim -1.8(-7.1 \lesssim \varepsilon \lesssim -1.8)$ eV, Cr 3d weight with the t_{2g} symmetry at $-1.7 \lesssim \varepsilon \lesssim 0.7(0.7 \lesssim \varepsilon \lesssim 2.6)$ eV, and Cr 3d weight with the e_g symmetry at $1.7 \lesssim \varepsilon \lesssim 4.0(2.9 \lesssim \varepsilon \lesssim 5.1)$ eV. The hybridization between the O 2p and Cr 3d bands is significantly large. The Fermi level is located at a deep valley of the t_{2g} majority-spin band while it is located in the energy gap between the O 2p and Cr 3d t_{2g} bands in the minority-spin band. Thus, the half metallicity of this material is evident in the calculated DOS.

The calculated orbital-decomposed partial DOS, $\rho_\alpha(\varepsilon)(\alpha=xy,yz,zx)$, in the Cr 3$dt_{2g}$ region are shown in Fig. [4], where the two components are exactly degenerate, $\rho_{yz}(\varepsilon)=\rho_{zx}(\varepsilon)$, for both paramagnetic and ferromagnetic states. The three t_{2g} orbitals are almost equally occupied by electrons in the paramagnetic state. In the ferromagnetic state, however, the d_{xy} orbitals is almost fully occupied by electrons, and therefore holes are only in the d_{yz} and d_{zx} orbitals. Also, the d_{xy} component has a rather high peaklike structure at ~0.7 eV below the Fermi level, indicating an essentially localized character of the d_{xy} electrons. The d_{yz} and d_{zx} components, on the other hand, have a rather wide band spreading over $-0.2 \lesssim \varepsilon \lesssim 0.7$ eV around the Fermi level, indicating an itinerant character of the d_{yz} and d_{zx} electrons. Here, the admixture of the 2p_z state of O(2) is significantly large: it occurs between the 2p_z orbitals of O(2), and the d_{yz} and d_{zx} orbitals of its neighboring Cr ions (see Fig. [2]). These results suggest that the double-exchange mechanism[3] should work for the occurrence of ferromagnetism, as will be discussed further below.

C. Band dispersion

The situation may be clarified further if one observes the calculated band dispersion near the Fermi level. The result is
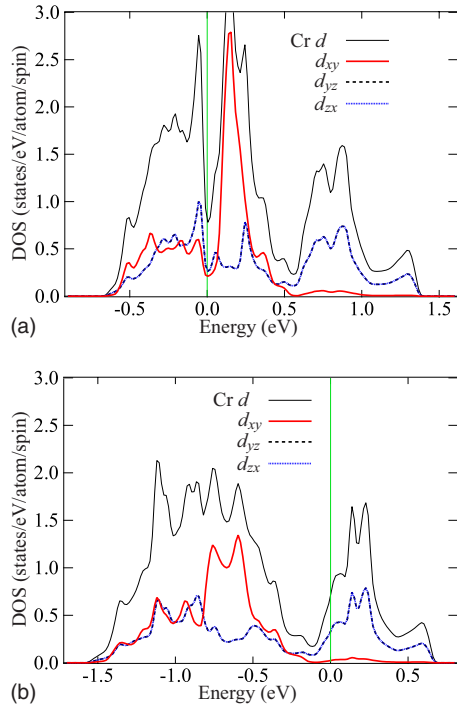
FIG. 4. (Color online) Calculated orbital-decomposed DOS [per spin per formula unit (f.u.)] of $K_2Cr_8O_{16}$ near the Fermi level for the (a) paramagnetic and (b) ferromagnetic states. The Fermi level is indicated by the vertical line. Contributions from the d_{yz} and d_{zx} orbitals (thin dashed and dotted lines) are exactly degenerate.

shown in Fig. 5. We find that a rather dispersionless narrow band of predominantly d_{xy} character is located at ~0.7 eV below the Fermi level, extending over a large region of the Brillouin zone. On the other hand, the dispersive t_{2g} bands of predominantly d_{yz} and d_{zx} characters with strong admixture of the $2p_z$ state of O(2) are located at $-0.2 \lesssim \varepsilon \lesssim 0.7$ eV, and cross the Fermi level. Thus, we have the dualistic situation where the essentially localized d_{xy} electrons at ~0.7 eV below the Fermi level interact with the itinerant d_{yz} and d_{zx} electrons of the bandwidth comparable with the intra-atomic exchange energy of ~1 eV, whereby Hund's rule coupling gives rise to the ferromagnetic spin polarization via the double-exchange mechanism.[3]

To support this further, we make the GGA+U calculation for the present material (of which the results are not shown here). We find that, as U increases, the d_{xy} band shifts further away from the Fermi level, leaving essentially no weight above the Fermi level, whereas the d_{yz} and d_{zx} bands with strong admixture of the O(2) $2p_z$ states are much less affected by the presence of U. These results are consistent with what is expected in the double-exchange mechanism of ferromagnetism. We point out that the situation is very similar to the case of CrO_2, which has so far been discussed in detail.[12–14]

Another aspect noted in Fig. 5 is that we have the semi-metallic band structure in the sense that the number of electrons is equal to the number of holes near the Fermi level (also see Fig. 6 below); there are 12 bands for the t_{2g} orbitals in the unit cell, which are fully spin polarized and are occupied by nine "spinless fermions," i.e., by nine up-spin (or
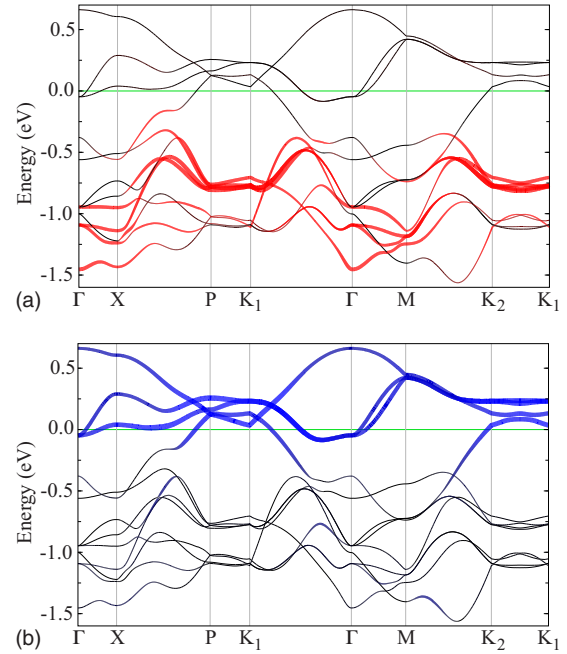

FIG. 5. (Color online) Calculated majority-spin band dispersion of $K_2Cr_8O_{16}$ near the Fermi level. There are 12 t_{2g} bands of the Cr 3d orbitals, three of which cross the Fermi level. The line width is in proportion to the weight of the d_{xy} component of Cr in (a) and to that of the $2p_z$ component of O(2) in (b).

majority-spin) electrons. The integer filling of spinless fermions can give rise to either semiconducting or semimetallic band structure, of which the latter is realized in the present system. This result suggests that the MIT observed in $K_2Cr_8O_{16}$ can possibly be a semimetal-to-semiconductor transition, where the band gap opens between the lower nine bands and upper three bands due to any unknown reasons. To realize this, however, we need the symmetry reduction (due to lattice distortion) because the band degeneracy between the third and fourth bands (counted from the top of the 12 t_{2g} bands) at the P point of the Brillouin zone cannot be lifted without breaking the fourfold rotational symmetry around the c axis of the tetragonal lattice. Without the lattice distortion, we could have a zero-gap semiconductor but the experimental data on the temperature dependence of the electrical resistivity[7] suggest that this possibility should be ruled out. Also, because no indications of this type of lattice distortions
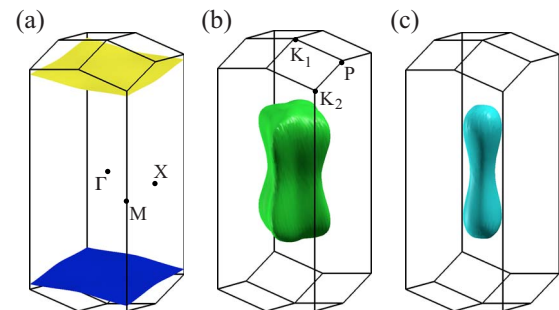

FIG. 6. (Color online) Calculated Fermi surfaces of $K_2Cr_8O_{16}$ in the ferromagnetic state. The 61st–63rd bands counted from the lowest are shown in (a)–(c), respectively.
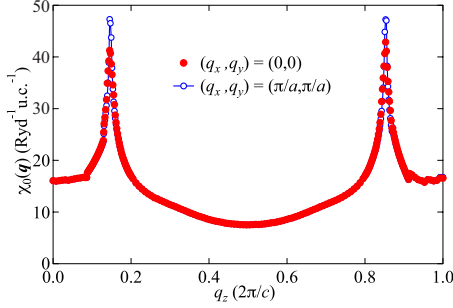
FIG. 7. (Color online) Generalized susceptibility $\chi_0(\boldsymbol{q})$ for the noninteracting band structure of $K_2Cr_8O_{16}$. Contribution from only the 61st band is shown.

at the MIT have been observed so far,[7] the semimetal-to-semiconductor transition seems to be unrealistic in $K_2Cr_8O_{16}$.

D. Fermi surface

The calculated Fermi surfaces of $K_2Cr_8O_{16}$ in the ferromagnetic state are shown in Fig. 6. There are 12 t_{2g} bands, three of which cross the Fermi level and form the semimetallic Fermi surfaces; i.e., the second and third bands (counted from the top) form the electron Fermi surfaces [see Figs. 6(b) and 6(c)] and the fourth band forms the hole Fermi surface [see Fig. 6(a)]. The wave functions at the Fermi surfaces have predominantly d_{yz} and d_{zx} characters with large admixture of the O(2) $2p_z$ states as shown above.

We find in Fig. 6(a) that there is a pair of the 1D-like parallel Fermi surfaces, which are seen to have a very good nesting feature. The nesting vector is aligned roughly along the Γ-K_1 direction and has the value $\boldsymbol{q}^* \simeq (0,0,0.147)2\pi/c$ or $(0,0,0.853)2\pi/c$ [a deviation in the (q_x, q_y) component will be discussed below]. Thus, the Fermi-surface instability corresponding to the wave number $\boldsymbol{q}^*$, leading to formation of the incommensurate long-wavelength (with a period of $\sim 7c$ in the real space) DW, may be relevant with the opening of the charge gap in the present material. Note that the spin and charge DWs occur simultaneously with the same wave number $\boldsymbol{q}^*$ since we have only the up-spin electrons.

E. Generalized susceptibility

To confirm the nesting features more precisely, we calculate the generalized susceptibility defined as $\chi_0(\boldsymbol{q}) = \Sigma_{\boldsymbol{k}}[f(E_{\boldsymbol{k}}) - f(E_{\boldsymbol{k}+\boldsymbol{q}})]/(E_{\boldsymbol{k}+\boldsymbol{q}} - E_{\boldsymbol{k}})$,[20] where $E_{\boldsymbol{k}}$ is the band dispersion and f is the Fermi distribution function at $T=0$ K. The calculated result is shown in Fig. 7, where the contribution from only the 61st band is given. Contributions from other bands including interband contributions are rather monotone functions of $\boldsymbol{k}$ over the entire Brillouin zone. Thus, the peak structure coming from the 61st band remains as a maximum even in the total susceptibility estimated in the constant matrix-element approximation.

To be more precise, the peak structure at $q_z^* = 0.295\pi/c$ and $1.705\pi/c$ seen in Fig. 7 remains strong, irrespective of the value of (q_x, q_y), although there is a small variation in the (q_x, q_y) plane. The true maximum appears at

$\boldsymbol{q}^* \simeq (\pi/a, \pi/a, q_z^*)$, or around $(\pi/a, \pi/a, q_z^*)$, splitting and deviating slightly from $(\pi/a, \pi/a, q_z^*)$ in the (q_x, q_y) plane. Thus, if we include the effects of electron correlations, the susceptibility can diverge at this momentum $\boldsymbol{q}^*$, resulting in the formation of the incommensurate long-wavelength charge and spin DW, which we hope will be checked by experiment in near future.

F. Metal-insulator transition

Now, let us discuss possible mechanisms of the MIT observed in $K_2Cr_8O_{16}$ at $T_c \simeq 95$ K. There are two types of scenarios: (i) correlation scenario where the electron correlations play an essential role and (ii) band scenario where the band structure solely determines whether the system is metallic or insulating. As a correlation scenario, we may have a possibility of the formation of the incommensurate long-wavelength charge and spin DW due to the Fermi-surface nesting as discussed above. This may give rise to the opening of the charge gap, resulting in the MIT observed in the present material. As another correlation scenario, we may have the charge ordering (CO) if the intersite Coulombic repulsions between charge carriers are sufficiently strong. In the present system, there may occur the localization of three spinless t_{2g} holes per four Cr site. We find that the possible spatial CO patterns are equivalent to those of $K_2V_8O_{16}$,[15–17] which results in the doubling of the unit cell along the c axis. As a band scenario, we may have the semimetal-to-semiconductor transition in the present system with the integer filling of spinless fermions as discussed in Sec. III C. Here, no spatial localization of carriers occurs but the band gap may open if the fourfold rotational symmetry around the c axis is broken due to lattice distortions, and the distortion is sufficiently large.

Although the lattice distortion is essential for the MIT in any of the above cases and its identification can specify which scenario is realized, no structural distortions associated with the metal-insulator transition have been observed so far.[7] This seems to suggest that the simple distortions such as the doubling of the unit cell along the c axis and the breaking of the fourfold rotational symmetry around the c axis may be ruled out. We therefore argue that the formation of the incommensurate long-wavelength DW, the observation of which is sometimes not very easy, may be relevant with the MIT in the present material. We hope that the anomaly at $\boldsymbol{q}*$ estimated above will be sought for carefully in future experiment.

Another experimental fact to be noted is that the spin polarization is hardly affected by the MIT in this material. This is interesting because the double-exchange mechanism for ferromagnetism (of which the energy gain occurs due to the first-order process of the hopping) should cease to work if the charge gap opens clearly in the majority-spin band and coherent motion of carriers vanishes. The double-exchange ferromagnetism may be killed in such cases. However, if the charge gap is small enough, the second-order processes of the hopping of conduction electrons can give rise to the ferromagnetic interaction between localized spins as well and thus the ferromagnetism can be maintained. The vanishing

first-order process seems to affect very little on the already fully spin-polarized system. Experimentally,[7] the electrical resistivity measurement shows that the temperature dependence is of a three-dimensional variable-range-hopping type rather than a thermal activation type and thus it is not clear whether the well-defined charge gap is present in this material. Also, the charge gap expected in the formation of the incommensurate long-wavelength DW state corresponding to q^* may not be so large. The observed saturated ferromagnetism maintained under the gap formation seems to be related to such situations.

G. Negative charge-transfer gap

We here point out that the present material K$_2$Cr$_8$O$_{16}$ is a doped negative charge-transfer-gap (CT-gap) type system[18] in the Zaanen-Sawatzky-Allen phase diagram.[19] Because K$_2$Cr$_8$O$_{16}$ is in the mixed-valent state, we need not invoke the negative CT-gap situation[18] for metallization of the system, as is realized in CrO$_2$ where the metallization via self-doping mechanism operates.[13] However, in a hypothetical K$_0$Cr$_8$O$_{16}$ system, where K ions are completely depleted and all the Cr ions are in the d^2 state, this self-doping mechanism should be relevant for both metallization and double-exchange ferromagnetism unless the strong electron correlations lead the system to a Mott-insulating ground state with spin $S=1$ local moments aligned antiferromagnetically or with local spin-singlet pairs of $S=1$ spins. We here point out that, even in K$_2$Cr$_8$O$_{16}$, the negative CT-gap situation is realized between the O(2) $2p$ and Cr $3dt_{2g}$ orbitals, as is evident in the calculated negative spin polarization of the O(2) ions. In fact, results of our GGA+U calculation for K$_2$Cr$_8$O$_{16}$ indicate that the gap in the DOS opens when U is large enough although the Fermi level is away from the gap due to the mixed-valent nature of the system. Thus, the deficiency of K ions, if realized experimentally, can offer an important opportunity for studying the negative CT-gap situation and its carrier number dependence.

IV. SUMMARY AND PROSPECTS

In summary, we have made the first-principles electronic structure calculations and predicted that a chromium oxide K$_2$Cr$_8$O$_{16}$ of hollandite type should be a half-metallic ferromagnet. We have shown that the double-exchange mechanism is responsible for the observed saturated ferromagnetism. We have discussed the possible scenarios of the metal-insulator transition observed at low temperature, which include possibilities of the formation of the charge order and semimetal-to-semiconductor transition, but we have argued that the formation of the incommensurate long-wavelength density wave of spinless fermions caused by the Fermi-surface nesting may be the origin of the opening of the charge gap. We hope that these predictions will be checked by further experimental studies.

Before closing this paper, let us discuss some prospects for future studies of this material, which may include the following:

(i) This material offers an interesting opportunity for studying the effects of the majority-spin band gap on the electronic properties of half-metallic ferromagnets. In particular, the so-called nonquasiparticle states[21,22] and the effects of the opening of the gap on the nonquasiparticle states should be pursued by the spectroscopic experiments such as photoemission and x-ray absorption experiment.[23–26]

(ii) The transport properties of K$_2$Cr$_8$O$_{16}$ are also anomalous,[7] as those of a "bad metal,"[22,27–30] which may also be interesting because not only the spin fluctuations but also the collective fluctuations of the orbital degrees of freedom between the degenerate d_{yz} and d_{zx} orbitals may play an important role.

(iii) Introduction of the deficiency of K ions, if it could be made experimentally, would enable us to examine the effects of changing the doping rate on the gap formation, double-exchange ferromagnetism, and half metallicity. We also point out that only the 1D-like Fermi surface should remain by ~10% hole doping if we assume the rigid-band shift of the Fermi level (see Fig. 5), suggesting the realization of the 1D electron system.

(iv) Theoretically, one should study the three-band Hubbard model with the d_{xy}, d_{yz}, and d_{zx} orbitals to see, in particular, the effects of orbital fluctuations on the electronic states of the system. The study may be extended to the d-p model including the $2p$ orbitals of O ions if one wants to take into account the negative CT-gap situation of the present system. Techniques beyond the GGA+U method, such as the dynamical mean-field theory[31] and variational cluster approach,[32] are required to examine the presence of nonquasiparticle states and their deformation due to the gap formation.

Finally, we want to point out that, because the basic electronic states of the present system have many aspects in common with those of CrO$_2$, it may be very useful to clarify similarities and differences in the electronic states between K$_2$Cr$_8$O$_{16}$ and CrO$_2$ in all the above respects.

Note added in proof. Recently, we were informed of a preprint of Ref. 7, where it was reported that the accurate temperature of MIT is 95 K and that no structural changes below this temperature have been observed yet.

[1] M. I. Katsnelson, V. Y. Irkhin, L. Chioncel, A. I. Lichtenstein, and R. A. de Groot, Rev. Mod. Phys. **80**, 315 (2008).

[2] It is also possible that only the minority-spin electrons form the Fermi surface with a gapped majority-spin band as in Fe_3O_4, see A. Yanase and K. Siratori, J. Phys. Soc. Jpn. **53**, 312 (1984).

[3] C. Zener, Phys. Rev. **82**, 403 (1951).

[4] T. Endo, S. Kume, N. Kinomura, and M. Koizumi, Mater. Res. Bull. **11**, 609 (1976).

[5] H. Okada, N. Kinomuraa, S. Kume, and M. Koizumi, Mater. Res. Bull. **13**, 1047 (1978).

[6] O. Tamada, N. Yamamoto, T. Mori, and T. Endo, J. Solid State Chem. **126**, 1 (1996).

[7] K. Hasegawa, M. Isobe, T. Yamauchi, H. Ueda, J. Yamaura, H. Goto, T. Yagi, H. Sato, and Y. Ueda (unpublished).

[8] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2k, An Augmented Plane Wave+Local Orbitals Program for Calculating Crystal Properties* (Technische Universität Wien, Austria, 2002); http://www.wien2k.at

[9] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[10] V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyzyk, and G. A. Sawatzky, Phys. Rev. B **48**, 16929 (1993).

[11] A. Kokalj, Comput. Mater. Sci. **28**, 155 (2003).

[12] K.-H. Schwarz, J. Phys. F: Met. Phys. **16**, L211 (1986).

[13] M. A. Korotin, V. I. Anisimov, D. I. Khomskii, and G. A. Sawatzky, Phys. Rev. Lett. **80**, 4305 (1998).

[14] A. Yamasaki, L. Chioncel, A. I. Lichtenstein, and O. K. Andersen, Phys. Rev. B **74**, 024419 (2006).

[15] M. Isobe, S. Koishi, N. Kouno, J. Yamaura, T. Yamauchi, H. Ueda, H. Gotou, T. Yagi, and Y. Ueda, J. Phys. Soc. Jpn. **75**, 073801 (2006).

[16] S. Horiuchi, T. Shirakawa, and Y. Ohta, Phys. Rev. B **77**, 155120 (2008).

[17] M. Sakamaki, S. Horiuchi, T. Konishi, and Y. Ohta, arXiv:0811.4338 (unpublished).

[18] D. Khomskii, arXiv:cond-mat/0101164 (unpublished).

[19] J. Zaanen, G. A. Sawatzky, and J. W. Allen, Phys. Rev. Lett. **55**, 418 (1985).

[20] J. Rath and A. J. Freeman, Phys. Rev. B **11**, 2109 (1975).

[21] D. M. Edwards and J. A. Hertz, J. Phys. F: Met. Phys. **3**, 2191 (1973).

[22] V. Y. Irkhin and M. I. Katsnelson, Phys. Rev. B **73**, 104429 (2006).

[23] T. Tsujioka, T. Mizokawa, J. Okamoto, A. Fujimori, M. Nohara, H. Takagi, K. Yamaura, and M. Takano, Phys. Rev. B **56**, R15509 (1997).

[24] D. J. Huang, H.-T. Jeng, C. F. Chang, G. Y. Guo, J. Chen, W. P. Wu, S. C. Chung, S. G. Shyu, C. C. Wu, H.-J. Lin, and C. T. Chen, Phys. Rev. B **66**, 174440 (2002).

[25] D. J. Huang, L. H. Tjeng, J. Chen, C. F. Chang, W. P. Wu, S. C. Chung, A. Tanaka, G. Y. Guo, H.-J. Lin, S. G. Shyu, C. C. Wu, and C. T. Chen, Phys. Rev. B **67**, 214419 (2003).

[26] E. Z. Kurmaev, A. Moewes, S. M. Butorin, M. I. Katsnelson, L. D. Finkelstein, J. Nordgren, and P. M. Tedrow, Phys. Rev. B **67**, 155105 (2003).

[27] L. Ranno, A. Barry, and J. M. D. Coey, J. Appl. Phys. **81**, 5774 (1997).

[28] K. Suzuki and P. M. Tedrow, Phys. Rev. B **58**, 11597 (1998).

[29] I. I. Mazin, D. J. Singh, and C. Ambrosch-Draxl, Phys. Rev. B **59**, 411 (1999).

[30] S. M. Watts, S. Wirth, S. von Molnar, A. Barry, and J. M. D. Coey, Phys. Rev. B **61**, 9621 (2000).

[31] L. Craco, M. S. Laad, and E. Müller-Hartmann, Phys. Rev. Lett. **90**, 237203 (2003).

[32] L. Chioncel, H. Allmaier, E. Arrigoni, A. Yamasaki, M. Daghofer, M. I. Katsnelson, and A. I. Lichtenstein, Phys. Rev. B **75**, 140406(R) (2007).